A survey of the cupric complexes of several alpha hydroxy acids indicates that the stepwise dissociation of the hydroxyl groups is a general characteristic. For example, Pickering's (19) "Potassio-cupric Hydrogen Citrate" containing 5 atoms of potassium and 1 of copper is very likely the first complex, and his "Potassium beta-Cupricitrate" with 6 atoms of potassium and one of copper the second complex for this acid. Any study of the equilibrium constants of complex substances of this sort must therefore discriminate between the two kinds that occur in the different pH ranges. Potentiometric pH titration curves usually fail to show any distinct breaks however, and manifest a smooth slope characteristic of weak polybasic acids.

## CONCLUSION

Evidence pointing to a stepwise dissociation of the hydroxyl groups in complex formation between copper and alpha hydroxy acids is discussed. In general, as a result of this behavior two different simple cupric complexes may exist, each in a different pH range.

A modification of the mechanism for complex formation outlined by Smythe and Schmidt is proposed.

## LITERATURE CITED

1. Smythe, C. V. and Schmidt, C. L. A., J. Biol. Chem., 88, 241 (1930).
2. Smythe, C. V., J. Biol. Chem., 92, 233 (1931).
3. Wark, E. E., J. Chem. Soc., (1932), p. 41, and previous papers with Wark, I. W.
4. Mathiev, J. P., Bull. soc. chim., 1, 1713 (1934).
5. Dumanski, A. and Chalisev, A. A., Kolloid Z., 47, 121 (1929).
6. Urban, F. and Shaffer, P. A., J. Biol. Chem., 94, 697 (1932).
7. Ambler, J. A., Ind. Eng. Chem., 28, 1266 (1936).
8. Riley, H. L., and Fisher, N. I., J. Chem. Soc., (1929) p. 2006.
9. Pickering, S. U., J. Chem. Soc., 99, 1347 (1911).
10. Gabiano, P., Compt. rend., 184, 1059 (1927).
11. deMallemann, R. and Gabiano, P., Compt. rend., 185, 350 (1927).
12. Mathieu, J. P., Compt. rend., 195, 1017 (1932).
13. Hakamori, S., Science Repts. Tohoku Imp. Univ., 16, 825 (1927).
14. Packer, J. and Wark, I. W., J. Chem. Soc., 119, 1348 (1921).
15. Wark, E. E., and Wark, I. W., J. Chem. Soc., (1930) p. 2474.
16. Kahlenberg, L., Z. physik. Chem., 17, 589 (1895).
17. Bullnheimer, F., and Seitz, E., Ber., 33, 817 (1900).
18. Cox, E. G., Wardlaw, W., and Webster, K. C., J. Chem. Soc., (1936) p. 775.
19. Pickering, S. U., J. Chem. Soc., 97, 1837 (1910).

PALEONTOLOGY.-Clistocrinus, a new Carboniferous crinoid genus. ${ }^{1}$ Edwin Kirk, U. S. Geological Survey.
Through the kindness of Dr. G. H. Girty, of the U. S. Geological Survey, I have been given the opportunity of studying and describing an interesting new crinoid genus from the Carboniferous of South-

[^0]eastern Alaska. This genus, for which the name Clistocrinus is here proposed, belongs to a group of small crinoids of anomalous structure which in recent years has been found to have a wide geographical distribution and to range throughout the Carboniferous and up into the Permian. As now known, these crinoids have been found in the Visean (Lower Carboniferous) of Belgium and England, and the upper Mississippian of the United States, the Pennsylvanian (essentially the European Upper Carboniferous) of the United States and Alaska, the Permo-Carboniferous of Russia, and the Permian of Timor and the United States. Clistocrinus, coming as it does from the lower Pennsylvanian of Alaska, is of very great interest both on account of its geographic and stratigraphic position. Structurally Clistocrinus furnishes an intermediate form in the series of these crinoids as known.

## Clistocrinus, n. gen.

The genotype is Clistocrinus pyriformis, n. sp.
Before giving a description of the crinoid, certain points of terminology and orientation will briefly be considered in order to avoid confusion. The theca is composed of three circlets of plates. According to Wanner's usage these would be named, as in a dicyclic crinoid, infrabasals, basals, and orals, the radials being absent. For convenience in the present case I prefer treating the form as a monocyclic crinoid, calling the same circlets of plates basals, radials, and orals, respectively. According to Wanner's thesis, such a form as this is derived from a dicyclic crinoid with four circlets of plates by the elimination of one circlet, the radials. I believe the reverse is true and that the four-circlet type is derived from the three circlet by an intercyclic interpolation of a fourth ring of plates which become known as radials. Were this the only evolutionary possibility, Wanner's terminology would still be applicable. I think, however, that the median circlet of plates of the threecirclet type is potentially either a basal or a radial ring and feel that it is less confusing to use a nomenclature based on monocyclic structure in such crinoids as have the orals alternating with the plates of the second range. To all intents and purposes, irrespective of potential dicyclic structure, these crinoids are monocyclic. In orienting the theca I call the large hydroporebearing oral the posterior and arrange the other plates accordingly. Wanner also calls this oral posterior, but according to his interpretation it then would have a radial position in this form as in Acaraiocrinus, and the orientation of the dorsal cup would be arbitrary, his posterior "basal" being $36^{\circ}$ out of line with the posterior oral. The difference of orientation between Wanner and myself must be borne in mind when reading his descriptions. The large lateral opening lying in the radial-oral plane which has universally been called the anal opening may be such, but I doubt it. The opening piercing the posterior oral, which is probably the anal opening, I shall call the hydropore, a somewhat equivocal term but in conformity with current and past usage.

The following brief diagnosis of the genus will give the salient features of the form, the more detailed description being found under the description of the type species.


Figs. 1-8.-Clistocrinus pyriformis, n. sp. 1, plate diagram. 2, view from right posterior interradius showing the lateral opening. 3-5, views of same specimen revolving the specimen progressively to the left. 6, tegminal view. 7, basal view. 8, another somewhat smaller specimen, posterior view showing the position of the hydropore. Figs. $2-8$ are approximately $\times 6$.

The basal units are three in number, two large and of approximately equal size, the third much smaller. The small unfused basal is the left anterior, a normal position for monocyclic crinoids. The radials are five in number and vary somewhat in relative size. The right posterior and right anterior radials are invaginated to form the lateral opening. The posterior oral is the largest and is pierced by a hydropore. Although not clearly seen, the posterior oral and the right and left anterior orals alone meet at the center of the tegmen. This is a condition common to other genera of this group. The sutures between the orals are sinuous, very like Embryocrinus. The right posterior oral instead of holding a median position between the right posterior and right anterior radials does not touch the right posterior radial, the common suture between the posterior and right posterior orals falling directly above the lateral opening. The lateral opening lies in the right posterior interradius, unequally notching the right posterior and right anterior radials. The superjacent orals are not invaginated.

## Clistocrinus pyriformis, n. sp.

Of this species three adult specimens and three or possibly more younger individuals are available for study. The specimens are calcified and were found in a richly fossiliferous crystalline limestone. The sutures show clearly in the larger specimens.

The species is a small one, the holotype measuring 4.7 mm in height by 4.2 mm in diameter. The theca is subpyriform in shape. The sides of the dorsal cup diverge fairly rapidly to about two-thirds the height of the radials and then constrict somewhat at the plane of the radial-oral contact. The tegmen is a rounded dome, with a height about one-third that of the theca. The orals are somewhat flattened, giving the tegmen an obscurely facetted appearance, with the angles falling along the inter-oral sutures. The plates are finely punctate.

The basal units are three in number, the small unfused pentagonal basal being the left anterior. The other two are hexagonal in outline and subequal in size. The height of the basal cup of the largest individual is 1 mm and its maximum diameter 2.3 mm . The radials are subequal in size. They have a uniform height looking straight down upon them of 2.2 mm , except the anterior, which gives a measurement of 2 mm . The breadth of the plates at their upper margin is variable. The right posterior is the narrowest with a width of 1.8 mm , estimating the width by projecting the right posteriorright anterior suture upward through the lateral opening. The right anterior radial is the widest at the upper margin, with a breadth of 2.7 mm . Measurements for the other radials read as follows: ant., $2.3 \mathrm{~mm} ; 1$. ant., $2 \mathrm{~mm} ; 1$. post., 2.2 mm . The width of the radials at the base is more uniform, the r . post., r. ant., and ant. radials measuring 1.5 mm . In the 1 . ant. the width is 1.4 mm , and in the 1 . post. it is 1.2 mm . The orals are difficult to measure owing to curvature and indistinct sutures. The width of the plate at the base can be measured with fair accuracy, however. This dimension on the r. ant., l. ant., and l. post. orals is the same, 2.7 mm . The posterior oral is by far the largest, with a width of 3.3 mm , while the r. post. oral is narrower than the first three noted, with a width of but 2.5 mm . The apposed faces of the orals are coarsely crenulate, as in Embryocrinus and Coenocystis. The hydropore cannot be located with certainty in the larger specimen illustrated, but its probable situation is indicated in figure 6 and was drawn in mainly to identify the hydropore-oral. The hydropore shows clearly in the
specimen illustrated as figure 8 and in one other. In the specimen not figured the hydropore is much nearer the apex of the oral. The hydropore shows as a pit, rather than as elevated pimple, as is often the case. In the larger specimen the pit is surrounded by a smoothly rounded ridge.

The lateral opening is of relatively large size, having a maximum height of 0.9 mm and a width at the oral-radial plane of 1.2 mm . It lies in the right posterior interradius, unequally cutting into the right posterior and right anterior radials. Of the total width, approximately 0.8 mm lies within the right posterior radial and 0.4 mm within the right anterior radial. The opening does not cut into the superjacent orals as is the case in several genera. One would expect the lateral opening to be covered entirely by the right posterior oral. Such is not the case, however. The posterior oral extends beyond the median line of the right posterior radial and meets the right posterior oral at a point about midway of the lateral opening.

On the surface of the tegmen of the largest individual are irregular superimposed raised areas. When first seen these areas were thought to be extraneous growths. Being restricted almost entirely to the tegmen, apparently having the structure of crinoid stereom, and similar but smaller areas being found on other specimens, it seems probable that they are structures of the crinoid itself. As seen the surface of these areas is covered with irregularly disposed suboval to subcircular depressions. In general appearance the depressions are similar to the pits for the reception of epithecal brachioles in some of the more primitive cystids, but the resemblance is probably superficial. There would appear to be no reason for calcified exothecal extensions on crinoids of this type. The pits are sometimes thickly clustered and sometimes fairly well separated. It is difficult to render the structures in a drawing, even to the extent of delimiting the areas themselves. The outline shown in figures 2 to 6 are intended only approximately to give the general size and distribution of the areas. In general these patches of stereom are most numerous near the periphery of the theca and along the inter-oral sutures.

The areal distribution of the epithecal structures in the largest specimen shows an almost continuous peripheral band at the base of the orals, with the greatest development along the inter-oral sutures. A large patch lies directly above the lateral opening, extending on both sides of the post.-r. post. oral contact. It extends upward along the suture to about one-half the height of the orals. From this patch a narrow band extends to the right horizontally and just above the radial-oral plane to another large patch on the r. ant.-l. ant. oral contact. This patch is clearly defined, and its surface rises well above that of the orals. It extends upward to about two-thirds the height of the orals. From this patch a broad irregular band extends across the l. ant. and l. post. orals to slightly beyond the l. post.-post. oral suture. The band broadens somewhat at both the l. ant.-l. post. oral and l. post.-post. oral contacts. This band lies at times somewhat above the radial-oral plane.

In two other somewhat smaller individuals the surface of the theca is not as well preserved, but structures suggesting similar epithecal deposits can be seen. As shown the areas are discontinuous and much smaller than in the largest specimen. Here again the main concentration of superficial stereom is along inter-oral sutures. In two small specimens the plate sutures cannot be seen, and the separation of tegmen and dorsal cup must be made arbitrarily. The pits in these specimens are relatively large, and apparently the epithecal areas extend onto the dorsal cup.

The stem cicatrix is round and has a diameter of 0.5 mm .

Picked out of the broken limestone fragments, and associated with the large specimens of Clistocrinus pyriformis, are five small subovate to capsuleshaped specimens that appear to be the young of the crinoid. Broken out of a dark crystalline limestone and not subjected to weathering, it is not possible to see plate sutures in all of them. One can be reasonably certain of at least three of the specimens, however. The tegmen and dorsal cup can be recognized, and the lateral opening and the columnar attachment can be identified with a fair degree of certainty. A fourth specimen is so similar to the other three as to render its identification reasonably sure. The fifth and smallest specimen is of uncertain placement. All the specimens agree in having a height in excess of the diameter. In the smaller specimens the diameter is approximately 0.8 the height. With increasing age the diameter approaches 0.9 the height, and this appears to hold as an average for the larger specimens. The proportions of tegmen and dorsal cup appear to be reasonably constant. In the younger specimens the base is more rounded, however, and it is difficult to distinguish one end of the theca from the other.

Horizon and locality.-The locality as given by the collector, A. F. Buddington, is "Northwest end of large island at head of Saginaw Bay, Kuiu Island, on east side; 40 -foot bed of limestone intercalated in series of interlayered chert, slaty quartzite, and cherty limestone." Girty ${ }^{2}$ gives an extensive faunal list of the associated fossils and on page 116 gives his opinion as to the age of this and similar faunas. His conclusion was tentatively to make the fauna upper Mississippian in age, though recognizing strong Pennsylvanian affinities. At my suggestion, L. G. Henbest examined the foraminifera from this locality, and his general conclusion ${ }^{3}$ is that these fossils favor an assignment of the fauna to the Pennsylvanian. Girty ${ }^{4}$ holds that although the evidence for a Pennsylvanian age does not appear much stronger than in 1929, the evidence for a Mississippian assignment seems somewhat weaker. His general conclusion is "The Alaskan fauna, I am inclined to believe, will prove to be of Pottsville age, or at least early Pennsylvanian, but I cannot say that the proof is at present extant." There are two other crinoid genera in the material. Synbathocrinus is indeterminate as to age. The other is a small crinoid which, though not typical, would be referred to Delocrinus, a Pennsylvanian genus. On the whole it would appear best to consider the fauna lower Pennsylvanian in age.

Types.-The cotypes and other specimens studied are in the collections of the U. S. National Museum, No. 94441.

Structurally we see in Clistocrinus an intermediate evolutionary stage between the Mississippian Lageniocrinus and the Permo-Carboniferous (Russia) and Permian (Timor) Acariaiocrinus (Streptostomocrinus). In an--other paper I am redescribing Lageniocrinus, based on a study of de Koninck's type specimen of L. seminulum. In Lageniocrinus there is a lateral ("anal") opening notching the upper corners of the two plates of the second range, one below the hydropore-oral and the one to the right. The orals are in alignment with the plates of the second range. In Clistocrinus we find the orals shifted to the left relative to the plates of the dorsal cup, becoming

[^1]"interradial" in position. The lateral opening is larger and has migrated somewhat to the left. In Acariaiocrinus the orals are "interradial" in position, and the lateral opening has migrated still further to the left, holding a median position on the right posterior "radial."

In some of the genera of this group of crinoids it has been assumed that the orals could be opened and closed. There has been no evidence for this, but anyone handling the material would, I think, come to this conclusion. I have very good evidence in the case of Coenocystis. Here there are five suboval pits, each at the center of the distal face of a plate of the second range ("radial"). Above each pit is a cavity excavated in the superjacent orals and equally shared by them. At the proximal angles of the orals are apophyses that project downward and bear against the inner wall of the dorsal cup when the orals are closed. It is obvious that we have here an articulating structure of rather complex type. In the case of Clistocrinus we have two difficulties. One is that the inter-oral suture between the posterior and right posterior orals is in line with the large lateral opening, and the proximal corners of these orals involved have no bearing surface. Obviously with the corners lacking support and the total bearing surface cut down these plates would have poor but perhaps adequate articulating surfaces. The other difficulty is the presence of the patches of stereom partially covering the inter-oral sutures and effectively soldering the oral dome into an immovable unit. It is possible that these pitted areas of superimposed material were not laid down by the crinoid, but the evidence at hand seems in favor of such an explanation. An examination of 10 well-preserved specimens of Embryocrinus shows nothing comparable in that genus, nor has anything of the sort been seen in a number of specimens of Coenocystis, though here the preservation, owing to silicification, makes the evidence less satisfactory. The only thing to do is to await more material to confirm or disprove the apparent structure. It would be of great importance, however, to know that such a crinoid could function with its orals firmly closed. In such case it would appear necessary to consider the lateral opening as an oral opening. I favor this view.

Of great importance in the orientation of the crinoids of this group and the Allagecrinidae as well, and in some cases the only reliable criterion, is the evidence offered by the orals. This does not seem to have been recognized. The arrangement and shape of the orals seems to be invariable. The posterior oral is the largest. Often the hydropore can be recognized without doubt, but fortuitous pitting and secondary alteration of the surface of specimens as small as these may lead one astray. The posterior oral may, however, be recognized by its pentagonal outline, and careful examination will usually show its distal portion formed of two faces meeting at an obtuse angle. The right and left anterior orals are large, quadrangular in outline and make contact with the posterior oral with their obliquely truncated distal faces. The right and left posterior orals are relatively small, triangular in outline and do not reach to the center of the tegmen. A recognition of these facts should prevent the preparation of drawings and plate diagrams that show the orals as five subequal triangular plates or with the right and left anterior orals truncated in the wrong direction. A modification of this typical structure is found in Embryocrinus and possibly elsewhere. Here the apical portion of the posterior oral forms an obtuse re-entrant angle, with a median projection. The apical portions of the right and left anterior orals fit into the re-entrant and in this case are not obliquely truncated.


[^0]:    ${ }^{1}$ Published by permission of the Director, U. S. Geological Survey. Received January 28, 1937.

[^1]:    ${ }^{2}$ Girty, G. H., in Buddington, A. F., and Chapin, Theodore, Geology and mineral deposits of southeastern Alaska: U. S. Geol. Survey Bull. 800: 113. 1929.
    ${ }^{3}$ Personal communication, August 29, 1936.
    ${ }^{4}$ Personal communication, November 11, 1936.

